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CORROSION OF THE COPPER OF THE JUNIATA.

BY CHARLES E. MUNROE.

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On October 23, 1882, I received telegraphic orders from the Secretary of the Navy to proceed to New York and examine the Juniata, with the object of ascertaining the cause of the corrosion of her copper. On reporting there I found the Juniata in dry dock, and an examination of her copper showed that the immersed surface had become covered with a pale green, earthy-looking coating, which at the time had become dry in spots and blistered. Many of these blisters had split, and the coating had flaked off to such an extent that the floor of the dock was thickly strewn with them. While the outer surfaces of these scales were of an apple-green color, the inner was, in the main, of a copper-red color, though in some instances it was black. The surface of the copper where thus exposed was, in the main, of a copper-red color, but in some spots black. Where these black spots appeared they were imperfectly circular in shape.

In addition to this general action which had caused the incrustation over the entire wetted surface, it was found that several plates had been so corroded as to be nearly or completely perforated. Eleven sheets on the keel, and sixteen on the bottom, most of them below the turn of the bilge, were so badly corroded as to require removal, and there were many others which gave promise of being soon in the same condition. This corrosion did not involve the whole of the plate on which it existed, nor was every plate attacked, nor in most cases contiguous plates, nor did it, in any case observed, extend to the nails or about them. The action was so irregularly distributed about the bottom and on the surface of the plates attacked, that there

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could be little doubt that the cause at work was a purely local one. When corrosion had gone on to the extent described, the outline of the spot was irregularly circular in shape, and the areas decreased unevenly from the outer surface inward, giving to the perforation an irregular cone-shape of very wide angle, the sides of the cone being in steps. The copper at these points seemed to be laminated.

Further inspection showed that a portion of the copper on the keel, and all of the copper on the rudder, was covered with a greenish incrustation which was harder, firmer, and more coherent than that on the remainder of the ship, and that this copper was *wholly* free from any evidences of corrosion. The portion on the keel was mid-way fore and aft at the top of the keel. It was a goring-shaped section, and, roughly estimated, it was fifty feet in length, and tapered from eighteen inches wide midway to a point at either end. Although this strip was wholly free from local corrosion, yet sheets of copper below it, on the keel, and above it, on the hull, were corroded as described. So on the stern there were several corroded sheets, while the copper on the rudder, immediately adjacent, was free from all evidences of it. From their location it was evident that this copper on the rudder and the top of the keel had been subjected to the same conditions of exposure after immersion as the remainder of the copper on the immersed surface.

The history of the Juniata was officially given as follows: When she had received her suit of copper, she was removed from the dry dock and lay in the Wallabout, under the iron derrick, for about five months; she was then moved to the wharf at the foot of Main street, near Store No. 30, where she lay for one and a half months. From there she was moved to the ordnance dock, where she remained three days; again moved to the foot of Main street, where she lay for a day and a half, and then was taken into the dry dock again. This was two days before I reported in New York. The corrosion noted had consequently taken place during the six to seven months in which the vessel was lying in the Wallabout. The copper on the rudder and the goring-shaped section on the keel were said to have been a portion of the old suit of copper which had been put on at the League Island Yard many years before. The goring-shaped piece owed its form to the fact that the ship was "hogged," and when pieces were inserted to straighten up the keel, it was thought unnecessary to strip the old copper from the old keel.

My attention was next turned to the examination of the new, unused



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copper from which the copper for the Juniata had been taken. I first, while examining the bottom, inquired of the workmen if they had noticed any peculiarity in the appearance of the copper as they put it on, and I found that they had remarked upon the "picturing," as they termed it, which seemed to be unusual. I applied then for sheets of copper from the same batch, and found that a few remained in the storehouse. On inspection I found that this "picturing" of which the workmen spoke was in the form of irregularly circular black spots and streaks on the surface of the copper. My first impression was that these spots were probably due to the fact that during transportation moisture had gathered on the surface of the plates, and that this moisture had absorbed hydrogen or ammonium sulphide from the bilge gases of the ship in which they were transported, and that this had tarnished them; but on examining the spots by light reflected at a wide angle, and by the sense of touch, it seemed probable that the plates had been rolled since the spots were formed, since the lustre on the spots was quite as brilliant as elsewhere on the surface. This theory of staining was not credited in the Constructor's Department of the Yard, as it was generally understood that the sheets were in this condition when put aboard the transport boat.

I next directed my efforts to tracing up the history of the Juniata copper. I hoped to ascertain when it was received and where it was rolled; then from the marks upon the sheets to learn from what batch of copper it had come; then to follow up these cakes to the smelting works, and from this point determine the source and character of the ore from which it was made. With this knowledge of the source of the copper and the various processes through which it had passed, I hoped to discover the source of any physical or chemical imperfections which the sheets might contain; but at the outset I found that there were no marks upon these sheets of copper by which they could be identified, and that the different invoices received at the New York Yard were so mixed as to be indistinguishable. All that I could learn was that all of the sheathing used was rolled at the Washington Yard. Since such difficulties as have arisen in the case of the Juniata's copper are likely to recur, it will assist materially in discovering the source of the difficulty if the history of the copper is known. I would recommend that hereafter a full record of the copper should be kept, and that each sheet should be stamped in the upper left-hand corner with the number of the batch from which it comes. This mark will be preserved by the lap of the sheet above. That this is feasible is

shown by a sheet of the old copper, stripped some two years previously from the Brooklyn, after it had been some years in service, which bears distinctly the following mark in left-hand upper corner, "U. S. N. Y. W., 1866." Starting from this point it will then be possible to compile from the log-books of a ship such statistics regarding the time the copper has been in use, and the conditions to which it has been exposed, as will enable us to determine the average life of copper sheathing—an important fact about which there now seems to be considerable uncertainty.

I next examined the Wallabout, a crescent-shaped body of water, something over 400 feet wide, lying between the Navy Yard proper and the cob dock. With the flood tide the current passes through to the westward, and with the ebb tide it moves to the eastward. Emptying into it are three sewers. At the east end, opposite the ordnance dock, is the Williamsburgh sewer, which drains 2300 acres of improved property, a considerable part being covered by petroleum refineries, chemical works, sugar refineries, and the like. About 500 feet from the dry dock the Brooklyn sewer, which traverses the Navy Yard, empties into the Wallabout. This drains an area of about 550 acres of improved property largely covered by residences. Near Store No. 30 a small sewer empties which drains a portion of the Navy Yard; and near the west end of the Wallabout the Hudson-avenue sewer, which drains 472 acres of Brooklyn, empties. The result of all this sewage flowing into the Wallabout is to modify very considerably the character of the sea water. The first effect observed is that which always takes place where sewage, charged with dissolved and suspended matter, flows into salt water—viz.: the precipitation of the suspended and dissolved matter and the formation of mud banks. This is going on continually in the Wallabout, and one of the largest banks was formed under the iron derrick where the Juniata lay for about five months. So shoal was it that she rested in the mud at low water, and in fact was probably imbedded in it for the greater part of the time. From this bank I gathered specimens of the mud, and I also got specimens of the bottom from off the ordnance dock. The first was regular dock mud, but the second consisted largely of coal tar. This last was accounted for by the existence, about opposite, of two large gas works, the "People's" and the "Nassau," while at the west end of the Wallabout there is a third. From the Williamsburgh and the Brooklyn sewers samples of sewage were taken. The color and character of the

sewage as it flowed from the sewers showed that the first was from factories, while the second was largely from dwellings. All the samples of sewage and mud were tested immediately after gathering, and all were found to be slightly *acid*. Naturally the character of the sewage flowing in, and consequently of the water in the Wallabout, will vary with the season, the day, and the state of the tide, so that the examination of only one set of samples is not of any value, except as indicating the character of the water at the time they were gathered. Realizing this, I applied to the Health Department of the city of Brooklyn, and also to Professor Charles F. Chandler, President Board of Health of New York, for information concerning the sewage emptying into the East River, but no investigation of this sort seems to have been made. Professor Chandler says, however, "There are a great number of petroleum refineries on Long Island at Hunter's Point and at Newtown Creek, and these refineries use enormous quantities of sulphuric acid, some portions of which find their way into the river. There are also chemical factories in Brooklyn—quite a number of them—and possibly their refuse materials are discharged from the sewers, by which the water along that shore may be rendered quite different from ordinary sea water." Through the courtesy of Civil Engineer F. C. Prindle, U. S. N., and Mr. J. H. Raymond, Commissioner of Health of the city of Brooklyn, I have obtained much of the information concerning the sewers which is given above. It would seem likely that considerable ammonia would reach the Wallabout from the gas works, were it not that ammonia has become so valuable an article, and the processes for recovering it from gas works have become so improved as to prevent much of it being allowed to escape. It is probable, too, that the considerable deposit of coal tar discovered at the end of the ordnance dock accumulated before these by-products of gas-making had become of any commercial value.

Besides the specimens of mud and sewage, one sheet of new copper from the lot from which the Juniata's copper was probably taken, five corroded sheets stripped from the Juniata, a strip of the copper from the rudder of the Juniata, and a sheet of the old copper which had been stripped from the Brooklyn when she was last recoppered here, were taken for examination.

Before leaving the Navy Yard I examined the pile of old copper stripped from the Brooklyn when she was last repaired. Although this had been in service many years (just how long I could not ascer-

tain), much of it was so strong that it drew out the nails in coming off. Some of the sheets were eaten through in much the same way as was seen in the Juniata's copper, but there were very few of them. Naval Constructor W. L. Mintonye, U. S. N., informed me that sheets of this old copper had been used for covering the anchor hoy used in the Wallabout, that these sheets had been in use thus for about two years, and that during that time the anchor hoy frequently rested on the mud banks, yet the copper was sound. Mr. Mintonye also described some experiments which he had made with the Juniata's copper. He took sheets from the lot with which the Juniata was sheathed, and coupled them in pairs by blocks of wood. At the time the Juniata was coppered he buried one of these pairs in the mud; the second was suspended six feet from the surface of the water, and the third was suspended at the surface of the water at low-water mark. These couples remained until the Juniata was docked in October, 1882. They were then taken out, and all were found unchanged except the couple buried in the mud, and these were only tarnished.

During my inspection of the bottom of the Juniata, I was accompanied by Chief Constructor T. D. Wilson, U. S. N., and he suggested in explanation of the corrosion that it was due (1) to iron coming in contact with the copper, and that this probably occurred while the Juniata was lying in the mud bank under the iron derrick, as it was rumored that iron chains and other iron articles had been lost in this mud bank from time to time. Since my visit to the Navy Yard this mud bank has been removed by dredging, but I cannot learn that any such articles have been recovered.

Another theory (2) advanced to account for the corrosion is that it was due to the sewage which flows into the Wallabout in such quantity. This was evidently in mind when my orders were drawn, as they read: "Your attention is called to the fact that a large sewer discharges into the Wallabout at a point near the wharf to which the Juniata has recently been moved."

Another (3) is that it was due to impurities in the copper, arising either from imperfect refining, impure ores, or the intentional admixture of foreign and cheaper metals.

Another (4) is that it was due to iron removed by abrasion, or in the form of rust, from the rolls in the rolling mill.

Another (5) is that it was caused by the adhesion of coal tar.

Another (6) is that it was due to physical or chemical differences



in different parts of the copper, which were caused by the method of manufacture.

On the 6th of December, 1882, in obedience to orders I proceeded to Washington, and there examined the sheets of corroded copper from the U. S. S. Brooklyn which were sent from Rio Janeiro. The corroded sheets presented practically the same appearance as those from the Juniata. There was the same irregularly circular outline, and the corrosion was seen in all stages, from a roughened surface at the outer edge of the circle to a thin edge at the centre. Through the courtesy of the Chief of the Bureau of Construction, I examined the report of the condition of the Brooklyn, with the accompanying drawings. These sketches showed that there was no regularity in the distribution of the corrosion, though most of the corroded sheets were below the turn of the bilge.

On the 9th of December, in obedience to orders, I proceeded to New York to examine the U. S. S. Trenton, then in dry dock. On inspection I found her copper to be in a very sound condition, so far as local corrosion was concerned, the only corroded plates being six about each of the Kingston valves, one plate on the starboard side in contact with the stern being roughened, but not pierced, and one on the port side forward, just below and in contact with the ram. Besides these there were a few plates which had been indented and torn slightly, probably through colliding with some object. In addition I found that one sheet had been removed from the garboard strake on the port side, about 60 feet aft. I could not learn why this plate had been taken off.

The history of this copper, so far as I could gather it, is as follows: The Trenton was in commission in Europe for some years, and on her return in October, 1881, she was laid up at the New York Yard. I am informed by her commanding officer, Captain F. M. Ramsay, U. S. N., that when she was brought in she was laid alongside the iron derrick, and she was so heavily loaded that it was with great difficulty that she could be forced into the mud bank under the derrick. After lying there some time she was drawn out into the Wallabout, and from that time until she was put into the dry dock in December, 1882, she lay nearly opposite the mouth of the Brooklyn sewer. The conditions, then, to which her old copper was subjected were almost identical with those to which the Juniata's new copper was subjected, the chief difference being that as the Trenton was heavily loaded, while the Juniata was light, the Trenton probably sank much deeper in the mud bank than the Juniata did.

On December 20, 1882, in obedience to orders, I proceeded to Washington to inspect the rolling mill at the Washington Navy Yard, then in operation. Here I witnessed the operations of hot rolling and scaling, and my attention was particularly attracted to the latter process, as it did not seem to be complete, some portions of the scale being adherent after the removal from the bath, necessitating the cleaning of the sheet as completely as possible by mechanical means. As the treatment with the lye and acid was done in a very crude way, by rubbing on with a broom, this may account in a measure for the failure to entirely remove the scale or oxide. During my visit I was the recipient of courteous attentions from Commodore T. Pattison, U. S. N., commanding, and from Naval Constructor S. H. Pook, U. S. N., in charge of the rolling-mill, and the latter permitted me to take copies of letters, of recent date, from the managers of some of the principal rolling-mills in the country, from which I extract the following :

Park, Scott & Co., Lake Superior Copper Mills, Pittsburgh, Pa., say : " The rolls in our mills which have given the most satisfaction are semi-steam-chilled." " We are not experienced as to what action sea water may have on sheathing made with iron rolls."

C. G. Hussey & Co., Pittsburgh Copper and Brass Rolling Mills, Pa., state : " For rolling copper we use principally the chilled iron rolls, and as far as our experience has gone we find them well adapted for the work. We never knew of any iron from the rolls adhering to the copper, but black spots may be on the copper from imperfect removal of the scale or oxide. That is the only way we can account for black spots or marks."

Hendricks Brothers, New York, write : " We consider chilled-iron rolls the best for the purpose referred to, and when replacing any at our own works, do so with those of that description. The rolling of copper in iron rollers is not detrimental for sheathing, nor would they injure it in any way as regards the action of sea water. The black spots spoken of are not iron, but copper scale or oxide, and do not affect the quality. Copper may be of equal purity, but some are harder than others ; the latter are preferred for the sheathing for vessels, on account of the action of salt water upon it."

Pope & Cole, Baltimore, Md., write : " The only suitable material for the construction of rolls for rolling copper is *best iron, chilled*. The arrangements for rolling copper at the Washington Navy Yard are, in our judgment, so good that some time since we availed of permis-

sion from headquarters to make copies of the working drawings in your mill, with the purpose of constructing one here, upon your method, in place of our present mill. The methods and surroundings of rolling copper have nothing whatever to do with the action of sea water upon copper sheathing on vessels. The trouble in cases where copper sheathing has become *honeycombed* or *quickly worn thin* when in contact with sea water is attributable to the fact of the presence of a little silver in copper, which is quickly attacked by salt water. Copper for rolling can be procured which has no silver whatever in it—not a trace. The black specks or spots which you referred to are not iron: they are the oxide of copper. Copper and oxygen have a wonderful affinity for each other, especially when copper is hot or in a molten state. The oxide of copper, or, as known in commerce, “copper scale,” is easily removed from sheets by “pickling,” and ought to be wholly removed before your sheets are cold-rolled. If you will heat a piece of bright polished copper and then expose it for one moment to the atmosphere, it will so quickly absorb oxygen therefrom as at once to become as black as iron.”

During this visit I received the following information from the executive officer of the Powhatan. “The Powhatan was lying at the wharf of the Brooklyn Navy Yard, near the iron derrick, from November 15, 1879, to January 23, 1880, and from December 23, 1880, to March 24, 1881. Shortly after each of the above occasions of her stay off the Navy Yard she went into the dry dock, and upon examination the copper on the bottom of the vessel was found in perfectly good condition.” The conditions of exposure of the Powhatan evidently differed from those of the Juniata only in the fact that the latter was lying in the Wallabout during the summer months, while the former was there during the winter. This would to an extent probably modify the action.

On December 28, 1882, Commodore Pattison, U. S. N., sent me the following samples: Ingot copper, Pope & Cole; ingot copper, Hendricks Bros.; copper cake, Pope & Cole; copper cake from refuse copper refined at the Washington Navy Yard. The ingot copper from Pope & Cole was full of air-holes; the rest of the samples were sound, fine-grained, and quite free from air-holes or cavities, the specimen from the Washington Navy Yard being especially so.

On December 12, 1882, I received the following letter:

BUREAU OF ORDNANCE, NAVY DEPARTMENT,  
WASHINGTON CITY, *December 11, 1882.*

Professor CHARLES E. MUNROE, *Chemist, U. S. N. Academy.*

*Sir*:—In connection with the condition of the copper sheathing on the Brooklyn, I beg leave to say (as probably throwing some light on the subject) that the copper on the ferryboat Billow, at the Torpedo Station, put on in May last, is very badly pitted.

This metal was furnished by the Bureau of Construction and Repairs, and the following analysis made\* at the Torpedo Station shows that it contains foreign matters :

	Per Cent.
Copper .....	98.492
Lead.....	0.172
Arsenic .....	0.290
Nickel.....	0.102
Cobalt.....	0.010
Iron.....	0.570
Oxygen .....	0.240
Zinc.....	0.272
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Also traces of silver and antimony.

This copper may have been taken from the same lot from which the Brooklyn was coppered. The Bureau will be glad to make other analyses of copper, if desired. I am, sir, your obedient servant,

MONTGOMERY SICARD,  
*Chief of Bureau.*

In reply to my inquiry as to the conditions to which the Billow had been subjected, Capt. T. O. Selfridge, U. S. N., commanding the Torpedo Station, states that "the Billow never has been aground since the copper was put on, and that she has only been exposed to the action of pure sea water."

Learning that there had formerly been trouble from the water of Baltimore Harbor, I addressed a prominent shipbuilding firm there, and received the following reply :

BALTIMORE, MD., *December 14, 1882.*

C. E. MUNROE, *Professor, U. S. Naval Academy.*

*Dear Sir*:—Replying to your favor of 9th instant in reference to the corrosion of copper and metal on vessels' bottoms in Baltimore Harbor, we would state that previous to the stopping of the sugar refineries and the deepening of our harbor, all the steamboats whose landings were in the vicinity of the refinery or at the foot of the street where the sewage of the latter was discharged,

\* By Professor J. Fleming White.

suffered very much, and had to be docked for repairs or renewal of metal once each year, and in some cases at the refinery wharves twice in one year. The metal would be eaten worst at the water line around the nails in the seams of the plates. Some of the boats that used iron for protection against ice put it on in the fall and had to remove it in the spring, because it would be eaten away at the water line and interfere with the boats running. All these boats now run two, three and four years without docking, and, if they have pure copper on, we find it good after four years. We have some cases that we attribute to inferior metal. One we have just completed, the ship *St. Albans*, engaged in the Atlantic trade, metal been on twenty-six months, in active use eighteen months, honeycombed badly and had to be removed; should have lasted forty months. Yours respectfully, etc.,

WILLIAM E. WOODALL & Co.

In considering the case of the *Juniata* we must bear in mind that it is to be expected that copper sheathing will corrode in use, and that the peculiar advantage which it offers for keeping a ship's bottom clean is due to the fact that the copper is acted upon by sea water and forms a salt which, as it dissolves or scales, carries off the barnacles or seaweeds with it, and that this corrosion goes on over the whole immersed surface and continues throughout the whole period of immersion.

What takes place with sound copper in pure sea water will occur in any solvent in which the copper is immersed. If there is no contact with other bodies, solid or gaseous, and no marked currents formed in the liquid, corrosion will take place equally over the whole surface of the copper, though the speed of the corrosion may differ with the solvents.

What is peculiar about the corrosion of the *Juniata's* copper is that it was local and abnormally rapid. We will now take up the various theories proposed to account for this.

1 and 4. That it was due to contact with iron.

On January 22, 1824, Sir Humphry Davy said: "The rapid decay of the copper sheathing of His Majesty's ships of war, and the uncertainty of the time of its duration, have long attracted the attention of those persons most concerned in the naval interests of the country. Having had my inquiries directed to this important object by the Commissioners of the Navy Board, and a Committee of the Royal Society having been appointed to consider of it, I entered into an experimental investigation of the causes of the action of sea water on copper.

"It has been generally supposed that sea water had little or no

action on pure copper, and that the rapid decay of the copper on certain ships was owing to its impurity. On trying, however, the action of sea water upon two specimens of copper sent by John Vivian, Esq., to Mr. Faraday for analysis, I found the specimen which appeared absolutely pure was acted upon even more rapidly than the specimen which contained alloy; and on pursuing the inquiry with specimens of various kinds of copper which had been collected by the Navy Board and sent to the Royal Society, and some of which had been considered as remarkable for their durability, and others for their rapid decay, I found that they offered very inconsiderable differences only in their action upon sea water; and, consequently, that the changes they had undergone must have depended upon other causes than the absolute quality of the metal.

"When a piece of polished copper is suffered to remain in sea water, the first effects observed are a yellow tarnish upon the copper and a cloudiness in the water, which take place in two or three hours. The hue of the cloudiness is first white; it gradually becomes green. In less than a day a bluish-green precipitate appears in the bottom of the vessel, which constantly accumulates, at the same time that the surface of the copper corrodes, appearing red in the water, and grass-green where it is in contact with air."

Pursuing his experiments, Davy showed that there must be free oxygen present in water in order that copper might corrode, for "copper in sea water deprived of air by boiling or exhaustion, and exposed in an exhausted receiver or an atmosphere of hydrogen gas, underwent no change, and an absorption in atmospherical air was shown when copper and sea water were exposed to its agency in close vessels."

From his investigations Davy ascertained that when copper, in contact with a metal which was electro-negative to it, was exposed to sea water, the electro-negative metal was attacked, and the copper was free from corrosion until the other metal was destroyed; and he proposed to protect sheathing by this means. "In pursuing these researches and applying them to every possible form and connection of sheet copper, the results were of the most satisfactory kind. A piece of zinc as large as a pea, or the point of a small iron nail, was found fully adequate to preserve forty or fifty square inches of copper, and this wherever it was placed, whether at top, bottom, or in the middle of the sheet of copper; and whether the copper was straight, or bent, or made into coils. And where the connection between

different pieces of copper was completed by wires, or thin filaments of the fortieth or fiftieth of an inch in diameter, the effect was the same: every side, every surface, every particle of copper remained bright, whilst the iron or the zinc was slowly corroded.

"A piece of thick sheet copper containing on both sides about sixty square inches was cut in such a manner as to form seven divisions, connected only by the smallest filaments that could be left, and a mass of zinc of the fifth of an inch in diameter was soldered to the upper division. The whole was plunged under sea water; the copper remained perfectly polished. The same experiment was made with iron; and now after the lapse of a month, in both instances, the copper is as bright as when it was first introduced, whilst similar pieces of copper undefended in the same sea water have undergone considerable corrosion, and produced a large quantity of green deposit in the bottom of the vessel.

"A piece of iron nail about an inch long was fastened by a piece of copper wire nearly a foot long to a mass of sheet copper containing about forty square inches, and the whole plunged below the surface of sea water; it was found, after a week, that the copper defended the iron in the same manner as if it had been in immediate contact.

"A piece of copper and a piece of zinc soldered together at one of their extremities were made to form an arc in two different vessels of sea water, and the two portions of water were connected together by a small mass of tow moistened in the same water; the effect of the preservation of the copper took place in the same manner as if they had been in the same vessel." (*Phil. Trans.* 1824, p. 151.)

On p. 242 *Phil. Trans.* 1824 Davy gives a report of additional experiments on the protection of copper sheathing. He says: "Sheets of copper defended by from  $\frac{1}{40}$  to  $\frac{1}{1000}$  part of their surface of zinc, malleable and cast iron have been exposed for many weeks in the flow of the tide in Portsmouth Harbor, and their weights ascertained before and after the experiment. When the metallic protector was from  $\frac{1}{40}$  to  $\frac{1}{150}$ , there was no corrosion nor decay of the copper; with smaller quantities, such as from  $\frac{1}{200}$  to  $\frac{1}{400}$ , the copper underwent a loss of weight which was greater in proportion as the protector was smaller; and, as a proof of the universality of the principle, it was found that even  $\frac{1}{1000}$  part of cast iron saved a certain proportion of the copper.

"The sheeting of boats and ships protected by the contact of zinc, cast and malleable iron in different proportions, compared with that

of similar boats and sides of ships unprotected, exhibited bright surfaces, whilst the unprotected copper underwent rapid corrosion, becoming first red, then green, and losing a part of its substance in scales.

"Fortunately, in the course of these experiments it has been proved that cast iron, the substance which is cheapest and most easily procured, is likewise most fitted for the protection of copper. It lasts longer than malleable iron or zinc; and the plumbaginous substance which is left by the action of sea water upon it retains the original form of the iron, and does not impede the electrical action of the remaining metal."

In *Phil. Trans.* 1825, p. 328, Davy gave the results of his "Further Researches on the Preservation of Metals by Electro-Chemical Means." He said: "As long as the whole surface of the copper changes or corrodes, no such adhesions (barnacles, etc.) can occur; but when this green rust has partially formed, the copper below is protected by it and there is an equal action produced, the electrical effect of the oxide, submuriate and carbonate of copper formed being to produce a more rapid corrosion of the parts still exposed to sea water; so that sheets are often found perforated with holes in one part, after being used five or six years, and comparatively sound in other parts.

"There is nothing in the poisonous character of the metal which prevents these adhesions (barnacles, etc.). It is *the solution* by which they are *prevented*—*the wear* of the surface. Weeds and shell fish readily adhere to the poisonous salts of lead which form upon the lead protecting the fore part of the keel; and to the copper, in any chemical combination in which it is insoluble.

"In general, in ships in the Navy, the first effect of the adhesion of weeds is perceived upon the heads of the mixed metal nails, which consist of copper alloyed by a small quantity of tin. The oxides of tin and copper which form upon the head of the nail and in the space round it defend the metal from the action of sea water; and being negative with respect to it, a stronger corroding effect is produced in its immediate vicinity, so that the copper is often worn into deep, irregular cavities in these parts.

"When copper is unequally worn, likewise in harbors or seas when the water is loaded with mud or mechanical deposits, this mud or these deposits rest in the rough parts or depressions in the copper, and in the parts where the different sheets join, and afford a soil or



bed in which seaweeds can fix their roots, and to which zoophytes and shell fish can adhere.

"As far as my experiments have gone, small quantities of other metals, such as iron, tin, zinc or arsenic in alloy in copper, have appeared to promote the formation of an insoluble compound on the surface, and consequently there is much reason to believe must be favorable to the adhesion of weeds and insects."

Up to July, 1824, all Davy's experiments had been tried in harbor in comparatively still water, but soon after the protectors were tested on a steam vessel in the North Seas, and it was found that sheets of unprotected copper one foot square lost about 6.55 grains in passing at a rate of eight miles per hour in twelve hours; but a sheet of the same size defended by rather less than  $\frac{1}{500}$  lost 5.5 grains, and like sheets defended by  $\frac{1}{70}$  and  $\frac{1}{100}$  of malleable iron each lost 2 grains. These experiments show that there is a mechanical wear of the copper in sailing, and which, on the most exposed part of the ship and in the most rapid course, bears a relation of nearly 2 to 4.55. The copper sheets used weigh from 7000 to 8000 grains, and the balance would detect a difference of  $\frac{1}{100}$  of a grain in carrying this load.

Further experiments showed that when air was excluded from a vessel containing sea water in which iron and copper or other corrodible metals were immersed, no action took place, and that the addition of an alkaline substance, even in presence of air, was sufficient to arrest corrosion; but if the solution was *strongly* alkaline, then the electro-chemical action was reversed and the copper was corroded while the iron was preserved. The results of applying protecting masses of iron to coppered ships are cited, and the effect seems to have been advantageous; but no instance is given where it had been tested for any long period.

In closing he says: "The copper used for sheathing should be the purest that can be obtained; and in being applied to the ship, its surface should be preserved as smooth and equable as possible; and the nails used for fastening should likewise be of pure copper; and a little difference in their thickness and shape will easily compensate for their want of hardness."

In the *Comptes Rendus*, 59, 15; 1864, M. Becquerel reviews Davy's work, and records the work which he himself carried on at Toulon under the direction of the Minister de la Marine, which confirmed the views as to the protective action of iron on copper when immersed in sea water.

In the *Trans. Inst. Nav. Arch.* **10**, 166; 1869, John Grantham, Benjamin Bell, Charles Lamport, John Scott Russell and C. F. J. Young, all testify to the destruction of iron in contact with copper, and the latter quotes Faraday, Wood, Normandy, Selwyn and Siemens in support of his views. These conditions, however, only hold true for sea water in an acid or neutral condition. At the time of my visit to the Wallabout I found the water and mud slightly acid, and if this be the prevailing condition of the Wallabout, it is impossible that the corrosion of the copper could have been due to the presence of iron.

But while this relative action holds good for acid and neutral solutions in general, in most alkaline solutions, and especially solutions of the alkaline sulphides, the reverse is true, and the copper becomes electro-positive and is dissolved, while the iron remains unacted upon. Davy pointed this out in 1812 (*Chemical Phil.*, p. 148), and again in 1825 (*Phil. Trans.*, p. 339); and Faraday, in his *Experimental Researches in Electricity*, Vol. II, p. 86, gives tables of the electro-chemical series for different solutions which show these facts. In order to test these statements I made experiments, taking solutions of ammonium carbonate and Severn-River water, and ammonium sulphide and Severn water. In each of these I inserted a strip of iron and one of copper in contact with each other and allowed them to stand. In 24 hours there was evidence of corrosion on the copper, and in one case where the action had gone on for two months the copper was eaten off to the surface of the liquid, and copper was deposited on the iron. The solution contained 10 cm. of yellow sulphide of ammonia of the ordinary strength to 200 cm. of water, and during the time spoken of the solution was in an open flask in a dimly-lighted hood. No quantitative experiments were made, since it was not important for this research in the case of the ammonium carbonate, and in the case of the ammonium sulphide the coating of sulphide on the copper made it difficult to determine the loss with any degree of accuracy.

In determining if such a condition of circumstances could occur in the Wallabout, we may learn something from the examination of the sewage waters and mud. The sewage water taken at the mouths of the sewers was collected in patent-stoppered lager-beer bottles, which were carefully rinsed with the water to be collected. Although tolerably free from odor when collected, by the time they reached Annapolis they were highly charged with gases, which proved to be

largely sulphide of hydrogen and some sulphide of ammonium. Through the decomposition they had become much more turbid from suspended matter than when first collected. So great was the pressure upon the bottles that, though they were kept in a cool place, one of them burst under the pressure of the confined gases. The sewage had become alkaline when it reached Annapolis. I give below the analyses of these waters, filtered, and of the sedimentary matter, and I add an analysis of the Severn-River water, since I used this in some of the experiments. The analyses given hereafter are usually the mean of several:

	Parts in 100,000.			Ammonia.		Salt.
	Vol.	Non-vol.	Total.	Am.	Al. Am.	
Williamsburgh.....	261.6	583.6	845.2	.1420	.1250	385.5
Brooklyn.....	118.6	160.8	279.4	.0758	.0472	135.2
Severn.....	157.0	1236.0	1393.0	.....	.....	1054.7

#### SUSPENDED MATTER.

	Parts in 100,000.		Total.
	Vol.	Non-vol.	
Williamsburgh .....	31.2	84.0	114.2
Brooklyn .....	22.6	38.1	50.7

The result of such sewage as the above flowing into salt water must be, not only the production of mud banks, as stated above, but also the generation of hydrogen sulphide and alkaline sulphides, for the salt water contains calcium sulphate (in pure sea-water it will rise to 100 parts in 100,000), and when organic matter comes in contact with this, calcium sulphide is formed, which gives off its sulphur as hydrogen sulphide when it comes in contact with the carbon dioxide of the air. Ammonium sulphide will then be formed through reaction with the sewage.

#### MUD.

The mud was stored in new paint-kegs immediately after collecting, and on arrival here it was transferred to air-tight glass jars. When the mud from under the iron derrick was dried, it was of a bluish-white color and contained a considerable number of shells. It effervesced somewhat with acids, and when moistened it had a clay-like appearance. On drying, it gave off a slight offensive odor of animal matter. The mud from off the ordnance dock appeared, on drying, to be a mixture of blue mud with coal tar, and gave off the

odor of coal tar on drying. The mud from the iron derrick lost 15.23 per cent. of volatile matter on ignition, while the mud from the ordnance dock lost 24.51 per cent. When treated with ether, both yielded a yellow extractive matter, which on evaporation gave off an acrid odor. Both samples after exposure became alkaline.

We see, then, that in the sewage emptying into the Wallabout we have materials for the formation of ammonium and other sulphides, and that, although at the time of my visit there the water was acid to neutral, yet, under the varying conditions prevailing, it is possible there are times when it may be alkaline. Is it, then, probable that iron in alkaline solution was the cause of corrosion? I think not, and for the following reasons:

If iron had fallen into this mud bank, it is probable that owing to its greater relative weight it would sink through the soft mud to the bottom. Now, there was considerable difference in height between the corroded plates highest up on the hull and those on the keel, and if the Juniata touched bottom on the keel, the iron in contact with the higher plates must have been buoyed up. Since, however, there was room for the much heavier Trenton to get in, it is probable that the Juniata did not touch hard bottom. This argument may, however, be met by supposing that both the vessels lay on the flat of the bilge in a trough in the bottom of the Bay.

Another consideration is that the corrosion is too local for simple contact. None of the holes were over two inches in diameter, nor the roughened spaces about them more than eight inches. Now, copper is a good conductor, and with sheets as thick as these it seems strange that the action should be confined to so small an area. I do not lay much stress on this point.

What seems to me conclusive is that both the Powhatan and the Trenton lay in the same berth without injury, and that the copper on the rudder of the Juniata and the goring-piece on the keel were under precisely the same conditions as the remainder of the copper on the Juniata, and they were not corroded; and finally, that the copper on the Billow was corroded in a similar way without having been exposed to like surroundings.

2. That it was due to sewage. Since household sewage may contain sodium carbonate and hyposulphite from the soap used, and zinc chloride and bleaching powder from the disinfectants employed, I tested the action of these substances upon both copper and oxide of copper, the substances and the solutions being enclosed in stoppered bottles. The following are the results after seven months' action:

Copper and sodium hyposulphite—copper coated with sulphide—no copper in solution.

Copper oxide and sodium hyposulphite—no copper in solution.

Copper and sodium carbonate—copper coated with green carbonate—considerable copper in solution.

Copper oxide and sodium carbonate—faint trace of copper in solution—the copper oxide unchanged in appearance.

Copper and zinc chloride—deep green deposit of copper chloride on sides of bottle—copper bright.

Copper oxide and zinc chloride—no action.

Copper and bleaching powder—copper coated with bluish coat—copper in solution.

Copper oxide and bleaching powder—trace of copper in solution.

All of these substances act upon the copper, but the last two would be destroyed by the organic matter in the Wallabout, and the first two would probably not exist any length of time in their original condition. But granted that any of them were present and free to act, or that there were free acids or ammonia or ammoniacal salts present, could they produce such corrosion as took place on the Juniata? In my opinion not, because they would be dissolved in the water or in a layer at the surface, and would produce corrosion over the entire immersed portion of the copper or else at the water line, while that of the Juniata was purely local and confined to widely and irregularly separated spots.

3. That it was due to impurities in the copper arising from imperfect refining, impure ores, or the intentional admixture of foreign and cheaper metals.

In the paper by Davy quoted above, it will be seen that the presence of iron, tin, zinc, arsenic and the like, in small quantities, promoted the formation of insoluble scale on copper. In Pope and Cole's letter we see that they attribute corrosion to the presence of silver. This view was advanced by A. A. Hayes (*Am. Jour. Sci.* [2] **II**, 324). He says: "Some analyses I made, many years since, of sheathing copper which had long resisted the action of sea water proved the presence of one ten-thousandth part of silver. It was found that even this small portion of silver sensibly modified the chemical relations of the metals, and observations had indicated that the quality for sheathing was improved. Copper of this kind is frequently met with in commerce, and is derived from the Chilian ores of copper, which, although argentiferous, do not yield enough silver to render its separation economical.

"An occasion offered for again examining this subject, when the argentiferous native copper of Lake Superior was first refined and rolled by the Revere Copper Co., more than five years since, and the results have lately been obtained. Four suits of sheathing, for large merchant vessels, formed the subjects for observations, the metal being of uniform composition, as determined by assay of the clipping from many sheets. Two thousand parts of the alloy contained four parts of pure silver, or the standard ton of this country contained four pounds of silver (0.20 per cent.).

"A *proximate* analysis of this metal was also made, and it proved to be pure copper throughout, the mass of which, an alloy of silver and copper, was evenly distributed so as to form either a mixture or a compound alloy, in which one part of the copper is truly combined with the silver, and the other and larger part simply combines with the alloy. This is a very common constitution of alloys, in which two metals exist without any metalloïd occurring to disturb the simplicity of the union, and always indicates a careful purification of the metals.

"It was assumed as probable that the silver alloy would close the pores of the copper, which takes place with a tin alloy in bronze, and, in a mechanical way, confers durability. If, however, corrosion should take place, it was in accordance with observed cases that the silver alloy would act as a negative element, and the copper alone would be removed. How erroneous these inferences proved will be seen in the detail of the results.

"The Chicora was coppered January 9, 1847, taking 7392 pounds of metal, which was fastened by bronze nails. She was employed in trade to China, and wore her copper so rapidly that it was removed in March, 1849, 2628 pounds only remaining. In this case the sheets, after the usual operations, had been consolidated by 'cold-rolling.'

"The Serampore was coppered January 18, 1847, requiring 8447 pounds of 'cold-rolled' metal, secured by bronze nails. She sailed to China and home *via* Cape of Good Hope, and to the Pacific and home *via* Cape Horn, requiring new copper in March, 1850. The weight of the remaining copper was not ascertained.

"The Hamilton was coppered October 22, 1847, requiring 7706 pounds metal, secured by bronze nails. The sheets used were in the ordinary or annealed state. This vessel was employed in the India trade, and wore out her copper in August, 1849. The weight of the copper remaining was 3086 pounds.

"The Carthage was coppered November 26, 1847, requiring 8727 pounds 'cold-rolled' metal, fastened by bronze nails. She was employed in the India trade, and her sheathing was destroyed in August, 1849. The copper remaining weighed 5810 pounds.

"Omitting the case of the Serampore, where the corrosion cannot be determined by weight, we have the loss in every one hundred parts of metal, for the time of duration, thus: The Chicora, twenty-seven months, lost 64.45 per 100; the Hamilton, twenty-three months, lost 59.95 per 100; the Carthage, twenty-one months, lost 33.45 per 100.

"Allowing the same rate of corrosion, and taking the time as twenty-seven months for each: The Chicora lost 64.45 in 100; the Hamilton lost 70.38 in 100; the Carthage lost 43.00 in 100.

"In the cases of the Hamilton and Carthage we perceive the influence of the different processes of manufacturing the sheets on the durability of the copper. By the operation of 'cold-rolling' the surfaces of the sheets are rendered very compact, and in any corroding solution they bear a negative relation to the metal in the same sheets between these surfaces. Such copper is also always strongly negative to annealed copper in acid solutions until the hardened surfaces are removed; it then loses this relation. The Hamilton exhibits the greatest effect of sea-water action on the annealed alloy, while in the Carthage the protecting influence of the hardening surface was exerted nearly to the time her copper was removed. These observations establish the fact of the rapid corrosion of an alloy thus constituted, and show its entire unfitness for sheathing purposes.

"The average duration of copper sheathing decreases slightly as the requirement of greater speed in sailing is more urgent. Taking one hundred merchant ships, sailing on different oceans, the average duration now on American ships is three years.

"On the point of the *kind* of corrosion following the exposure of the alloy to sea water and air, the information obtained of these trials is of a definite character. Part of the sheets remaining, and an ingot of the copper from smelting a large quantity, were assayed, and the results showed that the same proportion only of silver remained as was originally contained in the alloy. The silver, therefore, by taking the negative state in the mass of the metal alloy hastened its destruction, while its own form and condition were such that it separated as the copper was corroded."

In this connection I made the following analyses. In these analyses I designate the copper from the rudder of the Juniata as "rudder copper," that taken from the Juniata after corrosion as "old Juniata copper," that taken off from the Brooklyn, in order to put on her present suit, as "Brooklyn copper," and the new sheet from the New York storehouse as "new Juniata copper."

In the analyses of the coppers, I have followed the methods given by Andrew A. Blair, chemist to the United States Board for Testing Metals, which appear as an appendix to Ex. Doc. 98 of the Forty-fifth Congress, Second Session; and I have also employed the method of W. Hampe, given in *Zeitschrift für Analytische Chemie*, 176, 1874, and in Watts' *Dictionary of Chemistry*, Vol. VIII, Part I. The methods have sometimes been modified in a measure, to accommodate them to the appliances at hand. In the table, the "rudder copper" is No. 1; the "Brooklyn," No. 2; the "new Juniata," No. 3, and the "old Juniata," No. 4. The results given are the mean of a number of determinations:

	1.	2.	3.	4.
Copper,	99.428	99.225	98.426	98.509 per cent.
Silver,	.125	.085	.005	.010
Arsenic,	trace.	none.	.135	.159
Antimony,	none.	none.	.008	.005
Lead,	.010	.080	.178	.152
Iron,	.183	.252	.650	.580
Nickel,	none.	none.	.050	.010
Zinc,	none.	none.	.170	.150
Bismuth,	.005	.003	.012	.015
Oxygen,	.155	.185	.280	.235
	<hr/> 99.906	<hr/> 99.830	<hr/> 99.914	<hr/> 99.825

For comparison with these, I have sought to obtain analyses of different American coppers from the principal sources, in order that we might determine what would be termed "pure copper" in commerce here, but I have been unable, as yet, to obtain such, so I give (1) an analysis of a "refined copper," from Oker, made by Hampe, and reported in Fresenius' *Quantitativen Chemischen Analyse*, 2, 527; 1882; (2) an analysis of a "refined copper" from Colorado, made by T. Egleston, Ph. D., and given in *Trans. of American Institute of Mining Engineers* for October, 1882; (3) an analysis of "ingot Lake Superior copper," Andrew A. Blair, *loc. cit.* 295.



	1.	2.	3.
Copper,	99.325	99.705	99.420 per cent.
Silver,	0.072	0.135	0.014
Gold,	0.0001	...	...
Arsenic,	0.130	0.091	none.
Antimony,	0.095	...	none.
Bismuth,	0.052	...	none.
Lead,	0.061	none.	trace.
*Iron,	0.063	0.031	0.013
Cobalt,	0.012	...	...
Nickel,	0.064	...	...
Sulphur,	0.001	trace.	...
Oxygen,	0.1166	...	...
Tellurium,	...	0.083	...
Zinc and nickel,	...	0.024	...
Suboxide of copper, ...	...	...	0.537
Carbon,	...	...	0.041
	<hr/> 99.9917	<hr/> 100.069	<hr/> 100.025

The Juniata copper, then, is not so pure as the rudder copper or the Brooklyn copper, or the copper last cited. The excess of silver in the rudder and Brooklyn coppers may at first excite remark, but we must remember that both of these coppers had been exposed to sea water for a very long time, and that sea water contains chloride of silver in solution, and that silver will be deposited upon copper under these circumstances. Mulder, in his *Die Silber-Probirmethode*, 27, states that chloride of silver is soluble in solutions of all the metallic chlorides which are soluble in water. Watts' *Dictionary of Chemistry*, 5, 271, states that silver has been detected in sea water, and refers to *Ann. Ch. Phys.* [3] 27, 129, which I have not been able to consult, and T. Sterry Hunt, *Chem. and Geol. Essays*, 231, repeats this statement. To test it, I placed some freshly precipitated and

\* In examining the copper for iron, I deemed it important to test the nitric acid used, although it was bought, as chemically pure, through Desaga, of E. Merck, of Darmstadt. The first bottle examined was but partially full, and had been standing for some time in strong sunlight, and was evolving nitrous fumes, notwithstanding that the glass was of a dark green color. Analysis showed it to contain .00135 gram of iron in 100 cm. Another full bottle of the same lot, which had been standing in the dark, was tested, and was found to be free from iron. This last was used in the analyses.

washed chloride of silver in Severn water and inserted a strip of copper. In twenty-four hours a decided coating of silver was deposited on the copper.

The amount of silver present in the Juniata coppers seems, however, too small to have been the source of this trouble, and of the other substances found, the oxygen appears the one most likely to have been the cause of the trouble. It should be said that the darker, spotted portions of the new sheets were taken for analysis, and that on especially removing the surface from some of these spots by the aid of a bright steel file-scraper, I found it to consist of a film of oxide free from sulphide. But as from the first my attention and that of others had been called to this unusual feature in the copper, and as these spots closely resembled the corroded spots in form, it seemed proper to select these portions. I am not, however, assured that the oxide originally existed in the copper.

The following experiments were made to ascertain if corrosion would take place between copper and copper oxide in the presence of the materials in the Wallabout. Heavy, cold-drawn copper wire was cut into pieces. Each piece was then bent, and one end was heated in the flame until it was coated with oxide. The strips were then immersed in the solutions or buried in the mud, as given in the table below. We then had an electro-chemical couple with copper and oxide of copper. In the experiments cited below, No. 5 and No. 6 were the most satisfactory as regards the cleanliness of the copper after removal from the solution and washing :

Substance Used.	Loss.	Remarks.
1. Copper and Williamsburgh sewage.	1.42 per cent.	Liquid alkaline—contained coal tar.
2. Copper oxidized and Williamsburgh sewage .....	1.45   “	Liquid alkaline—contained coal tar—copper pitted.
3. Copper and Brooklyn sewage.....	3.42   “	Liquid faintly alkaline.
4. Copper oxidized and Brooklyn sewage.....	2.99   “	Liquid faintly alkaline—copper pitted.
5. Copper and mud from under shears and Severn water.....	7.24   “	Liquid faintly alkaline—no pitting.
6. Copper oxidized and mud from under shears and Severn water...	14.64   “	Liquid faintly alkaline—copper badly pitted.
7. Copper and mud from Ordnance Dock and Severn water.....	4.06   “	Liquid alkaline—no pitting.
8. Copper oxidized and mud from Ordnance Dock and Severn water....	3.06   “	Liquid alkaline—copper faintly pitted.

As in these cases the solutions were all slightly alkaline, I repeated the experiments with Severn-River water, and with common-salt solutions, and in each case the copper was corroded. In addition, I connected my couple with a galvanometer and got a marked deflection of the needle. Hence there can be no doubt that electrochemical action can go on between copper and copper oxide in sea water. This view is supported by the fact that all authorities are agreed that the corrosion of pure copper by pure sea water cannot take place in the absence of air. This air supplies oxygen, and the first step in the process of corrosion is one of oxidation. If, then, the copper be oxidized when immersed, the process is facilitated.

5. That it was caused by the adhesion of coal tar. In the examination of the Juniata, no coal tar was observed in contact with the corroded spots, though small amounts were noticed elsewhere, the copper at those points being sound. In the experiments last cited, when coal tar was present it adhered to the copper so firmly that it was difficult to remove it, and it formed a strongly adherent varnish or lacquer which seemed to protect the copper from corrosion.

6. That it is due to physical or chemical differences in different parts of the copper which were caused by the method of manufacture. From the consideration of all the circumstances, and especially of the facts that the copper is found to be *spotted* with oxide; that these spots are irregularly distributed over the plates; that they generally agree in configuration and size with the corroded spots, and that the copper at the corroded spots appears laminated, I am led to conclude that this theory is the more probable one, and that the imperfections result from blister-holes in the copper and the incomplete removal of the scale.

We have found that in the existence of these spots of scale or oxide we have a condition which is favorable to the commencement of the corrosion. Why does it continue?

If we examine one of the corroded spots from which the surface has been removed, we find that the remaining surface is roughened. Now, such a surface is more readily attacked than a polished surface. This latter is a well-known fact in connection with the "rusting" or corrosion of metals, and it is for this reason largely that metal articles are polished. But it seems to me that there is an additional reason for action at this point. In the *Proc. Nav. Inst.* 8, 502 I have shown that annealed steel is much more soluble in sea water than "tempered" or hardened steel, and that when in contact the soft metal is rapidly



corroded. I have recently been confirmed in the truth of my observations by the investigation of M. Gruner in *Comptes Rendus*, 96, 195. I am inclined to the opinion that the same holds true of copper of varying hardness, and I find support for my opinion in the statement of A. A. Hayes.\* I believe that the copper beneath the spots of scale is softer than that about it, and furnishes the differences necessary for this action.

My theory to account for the existence of these differences and for the formation of the spots is as follows: I assume that an unsound cake of copper is taken for rolling which contains cavities like those seen in the ingot from Pope & Cole. When this is rolled into a bar, the cavities will be extended in the direction of the length of the bar. When the pieces of bar are afterwards rolled into sheets, these cavities will also be extended in the direction of the width of the sheet. These changes in form would of course be irregular, and would tend to produce such shapes as were seen on the copper. These cavities would necessarily contain gas, and copper is a very excellent conductor of heat, while gases are as a rule very poor conductors. Then, when the whole is heated and allowed to cool, the space about the cavity would be longer in cooling than the remainder, and, as a consequence, more scale would be formed at that point than elsewhere, and might adhere more firmly, or its formation might continue after the scaling process was considered complete. This layer of oxide and cushion of gas would then prevent the copper at this point from becoming as hard, through rolling, as over the remainder of the surface. The fact that the copper appears slightly laminated at some of the corroded spots seems to substantiate this theory. It may be objected that an enclosed gas at the high temperature of the operation would exert pressure sufficient to burst the envelope, but we must remember that the cavities were formed when the gas was at the temperature of molten copper.

In conclusion, I would state that in my opinion the corrosion of the Juniata's copper was due principally to the presence of spots of oxide of copper on the surface of the plates at the time they were put on, and I would recommend in the future the use of a pure copper, care in the production of sound cakes, and careful removal of the scale.

\* *Loc. cit.*

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